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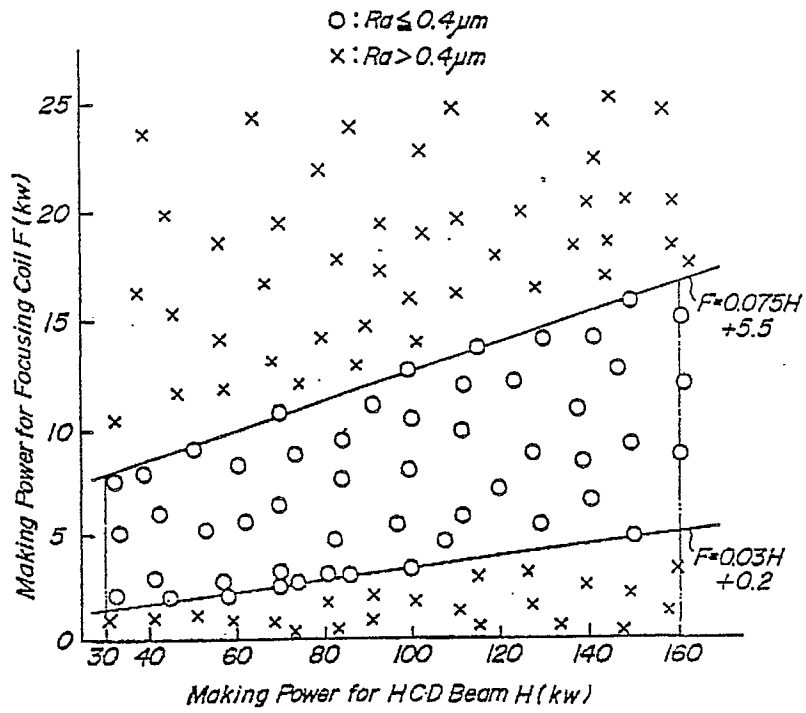
54 **STEEL SHEET HAVING DENSE CERAMIC COATING WITH EXCELLENT ADHESION, SMOOTHNESS AND CORROSION RESISTANCE AND PROCESS FOR ITS PRODUCTION.**

57 A process for coating the surface of low-carbon steel sheet or stainless steel sheet with a ceramic coating, which comprises extending a focusing coil which serves as a path for migration of an evap-

orated substance as far as the vicinity of the surface of the steel sheet, providing a metal-semimetal coating composed of at least either a metal or a semi-metal as an undercoat layer, and forming thereon at

least one layer of ceramic coating to obtain ceramic-coated steel sheet having excellent adhesion, smoothness and corrosion resistance.

FIG. 3



TITLE MODIFIED
see front page

Specification

STEEL SHEETS PROVIDED WITH DENSE CERAMIC COATING
HAVING IMPROVED ADHESION PROPERTY, SMOOTHNESS AND
CORROSION RESISTANCE AND METHOD OF PRODUCING THE SAME

TECHNICAL FIELD

This invention relates to a method of forming a ceramic coating having rich adhesion property, smoothness and corrosion resistance onto a surface of a low carbon steel sheet, a stainless steel sheet or the like.

BACKGROUND ART

Recently, the coating technique using plasma is considerably advancing and widely used in various fields. As the use of such a coating technique, there are mentioned, for example, formation of magnetic recording thin films, various abrasion resistant coatings, corrosion resistant coatings, decorative coatings, far-infrared ray heating elements and the like.

In general, evaporation substance of metal, semi-metal or the like can be ionized or activated to give high motion energy by utilizing the plasma, whereby sheets having good adhesion property between vapor deposited film and substrate and film quality are obtained.

Heretofore, there have been magnetron sputtering method, EB (electron beam) + RF (radio frequency)

method, plasma CVD method and the like as the plasma coating method, and multi arc method using vacuum arc and ion plating using hollow cathode discharge (HCD) method are recently known.

Among these plasma coating methods, the hollow cathode discharge method is relatively high in the ionization ratio and the film forming rate, so that it is utilized for small size ceramic coatings such as decorative articles, tools and the like.

In order to form ceramic coating having improved properties such as adhesion property, uniformity, corrosion resistance and the like onto a surface of steel sheet having a large surface area by these methods, it is necessary to increase the ionization ratio in the ion plating or ion plantation treatment, to increase the voltage applied to the steel sheet and to raise the temperature of the steel sheet.

In the coating film obtained by such a treatment, the film quality, adhesion property and corrosion resistance are largely improved, but it can not be said that satisfactory adhesion property and corrosion resistance are obtained, and hence it is demanded to more improve these properties.

Particularly, the ion plating treatment through the hollow cathode discharge method can expect the improvement of corrosion resistance, decorative property

or wear resistance on steel sheets having a large surface area for use in building materials or the like, so that the utilization thereof is attempted, but it is not yet put into practical use at the present.

Because, such a steel sheet is required to have the following conditions:

- 1) the adhesion property between steel sheet and ceramic coating is good;
 - 2) the ceramic coating can uniformly be coated over a large surface area;
 - 3) the film quality (particularly densification) of the ceramic coating is good;
 - 4) the corrosion resistance is excellent;
 - 5) the coating can be formed on the steel sheet having a large surface area at a high speed and under good plasma atmosphere; and the like,
- but the above conditions could not sufficiently be satisfied by the conventional hollow cathode discharge method.

Apart from this, there are recently made investigations on the properties of surface-treated steel sheets through ion plating using the arc discharge method, and consequently it is reported that when a different metal is subjected to dry plating at an interface of the steel sheet to form a double layer coating, the corrosion resistance is considerably

improved as compared with that of the single layer coating. {see Tetsu to Hagane, 72(1986), S1309 by Hiroshi Kagechika, Hiroshi Kibe, Takeshi Aniya, Hiroshi Naemura, Takashi Haratomi}. On the other hand, Japanese Patent laid open No. 62-99458 discloses a method consisting of a first step of conducting ion plating under a high vacuum atmosphere of not higher than 1.0×10^{-5} Torr to form a first plated layer and a step of forming a plated layer of a different material from the first layer on the above layer. This ion plating method is required to use a high vacuum that an atmosphere pressure under vacuum is not higher than 1.0×10^{-5} Torr, so that there is caused a problem when it is actually adopted in an industrial scale.

Furthermore, it has lately been reported that the corrosion resistance is improved by subjecting stainless steel sheet after the electrolysis with nitric acid to SiO_2 or Si_3N_4 coating through plasma CVD (Hashimoto et al: CAMP - ISIJ. Vol. 1 (1988), P426 and Japanese Patent laid open No. 63-62860). In this method, however, ion bombardment treatment is usually conducted before the dry plating treatment, so that the electrolytic effect on the surface of the steel sheet is disappeared to form a passivative film on the surface of the stainless steel sheet, and consequently the adhesion property between steel sheet and ceramic coating is

deteriorated and there are remained many problems to be solved when it is adopted in the actual production step.

In Japanese Patent Application Publication No. 55-33595, it has been attempted to adhere a substance having a good far-infrared ray radioactivity such as TiO_2 , ZrO_2 , Al_2O_3 or the like onto a surface of metal sheath type heating element as a far-infrared ray heating element suitable for use in a heat source for heating or drying, a reflective plate for a stove and the like. In this method, however, the difference in thermal expansion coefficient between heating element and ceramic coating is large, so that the ceramic as a surface layer is apt to be peeled off.

As a means for solving this problem, there is proposed a method wherein a ceramic heating element consisting mainly of conductive ceramic such as TiC , TiN , $\text{TiC-TiN-Al}_2\text{O}_3$ or the like is used instead of the metal sheath type heating element and the aforementioned far-infrared ray reflection type ceramic layer such as TiO_2 or the like is formed on the surface thereof as disclosed in Japanese Patent laid open No. 60-60990 and No. 60-130082. In this case, however, the coating method is spraying, immersion or heat treatment, so that it can not be said to be a basical countermeasure.

DISCLOSURE OF INVENTION

The invention advantageously solves the above

problems and is to provide a method of advantageously forming a dense ceramic coating having excellent adhesion property, smoothness and corrosion resistance when the ceramic coating is formed on low carbon steel sheet, stainless steel sheet or the like.

The inventors have made studies in order to solve the above problems, and as a result it has been found out that a focusing coil for guiding an evaporation substance into a substrate, which has hitherto been arranged only in the vicinity of an evaporation source, is extended near to the substrate to utilize an inside of such an elongated focusing coil as a passage for moving the evaporation substance and ion plating is carried out under condition that a power applied to HCD beam and focusing coil satisfies a given range, whereby a very dense ceramic coating is obtained and hence the adhesion property, smoothness and corrosion resistance are considerably improved.

The invention is based on the above knowledge.

That is, the invention lies in a steel sheet provided with a dense ceramic coating having improved adhesion property, smoothness and corrosion resistance, comprising an underground coating formed on a surface of a low carbon steel sheet or a stainless steel sheet and made from at least one of metals and semimetals, and a ceramic coating of at least one layer formed on said

underground coating; said ceramic coating having a surface roughness Ra of not more than 0.4 μm and a pore number per 1 cm^2 of not more than 1.

Furthermore, the invention lies in a method of producing steel sheets provided with a dense ceramic coating having improved adhesion property, smoothness and corrosion resistance by forming a ceramic coating onto a surface of low carbon steel sheet or stainless steel sheet through an ion plating treatment with HCD method, which comprises forming a metal-semimetal coating made from at least one of metals and semimetals as a first layer onto said surface of said steel sheet and forming a ceramic coating as a second layer on said coating under the following conditions using as a moving passage of an evaporation substance an inside of a focusing coil arranged so as to surround an outer periphery of a crucible and extend near to said surface of said steel sheet.

Account

$$30 \leq H \leq 160$$

$$0.2+0.03H \leq F \leq 5.5+0.075H$$

(wherein H: a making power (kW) of HCD beam

F: a making power (kW) of focusing coil)

In the invention, it is advantageous that prior to the formation of the metal-semimetal coating as a first layer, the steel sheet surface is subjected to a

polishing treatment so as to have $Ra \leq 0.4 \mu\text{m}$, or the steel sheet is preliminarily heated at 100-600°C, or further the steel sheet surface is subjected to Cr or Ni plating through a wet plating.

Furthermore, in the invention, a ceramic coating can repeatedly be formed on the ceramic coating as a second layer through the presence or absence of the metal-semimetal coating, if necessary.

Moreover, in the invention, it is advantageous that an annealing treatment is carried out at 500-1200°C in an oxidizing atmosphere after the formation of the ceramic coating as a final layer.

According to the invention, at least one layer selected from nitrides, carbides and carbonitrides of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Co, Ni, Al, B and Si and oxides of Al, Zn, Mn, Mg, Ti, Cr, B, Ni and Si is particularly advantageously adapted as the ceramic coating.

Thus, when the ion plating is carried out according to the invention, steel sheets provided with a very dense ceramic coating having not only adhesion property and corrosion resistance but also excellent smoothness of $Ra \leq 0.4 \mu\text{m}$ and further pore number per $1 \text{ cm}^2 \leq 1$ are obtained.

The invention will be described in detail below.

At first, the invention is described with

respect to experimental results succeeding the invention.

A hot rolled sheet (thickness 2.2 mm, width 500 mm) of a low carbon steel containing C: 0.044 wt% (hereinafter shown by % simply), Mn: 0.30%, P: 0.008% and S: 0.012% was cold rolled to a thickness of 0.3 mm, and then subjected to a recrystallization annealing at 750°C, and thereafter the steel sheet surface was degreased and a TiN coating was formed on the steel sheet surface by the following methods ①, ②, ③, ④, ⑤ and ⑥.

Account

- ① The coating formation was carried out by a so-called EB+RF method wherein Ti was evaporated by electron beam scanning and ionized with RF (Radio Frequency) coil to form TiN coating (1.0 μm thickness). Moreover, the treating condition was a vacuum degree of 6×10^{-4} Torr, and the EB (pierce type) irradiating conditions were acceleration voltage: 60 kV, current: 5 mA and RF power of 800 W. Furthermore, the preliminary heating temperature was 400°C and the applied voltage was 800 V.
- ② The coating formation was carried out by EB+RF method wherein Ti coating (0.5 μm thickness) was formed on the steel sheet surface by electron beam scanning and Ti was evaporated and ionized by RF coil to form a TiN ceramic coating (0.5 μm thickness). Moreover, the

treating condition of Ti coating as a first layer was a vacuum degree of 2×10^{-4} Torr, and the EB (pierce type) irradiating conditions were acceleration voltage: 60 kV and current: 5 mA. In the formation of TiN coating as a second layer, power of RF for ionization of N_2 gas was 800 W in the same EB conditions. The vacuum degree in the formation of TiN coating was 7×10^{-4} Torr, and the preliminary heating and applied voltage were the same as in the conditions of ①.

③ A TiN coating of 1 μ m in thickness was formed onto the steel sheet surface by using an ion plating apparatus of HCD system shown in Fig. 1.

In this drawing, 13 is a substrate, 14 an inlet of reaction gas, 15 a crucible, 16 an evaporation source (Ti), 17 a discharge port for high vacuum suction, 18 a vacuum tank, and 19 an HCD gun.

The HCD gun is a combination of an outer layer 19-1 made from graphite and an inner layer 19-2 made from Ta in this embodiment, wherein the outer and inner layers are separated from each other at a certain space. Furthermore, in order to prevent discharge between layers, current can be flowed from the inner layer 19-2 to the evaporation source inside the crucible 15 though the illustration is omitted. Thus, the abnormal discharge of the HCD gun becomes less and the long life of HCD gun is attained.

Furthermore, the HCD gun 19 is always held at a constant distance to the crucible 15 by means of a feed mechanism 19-3, whereby the supply of stable plasma beam can be ensured over a long period of time. Moreover, 19-4 is a power source for HCD gun and 19-5 is an inlet for Ar gas.

Further, 20 is a focusing coil arranged around the HCD gun 19. The generated plasma is focused into a fine plasma beam 21 by the focusing coil 20. Then, the focused fine plasma beam 21 is deflected so as to bend in a direction perpendicular to the surface of the evaporation source as shown by dotted lines in the drawing by means of a focusing coil 22 arranged around the crucible 15 acting to change the magnetic field from up direction to down direction and irradiated the evaporation source. By the irradiation of the perpendicularly bent plasma beam, the evaporation source is evaporated just above, whereby the uniform deposition of the evaporated substance to the substrate can be achieved.

In this case, the focusing coil 22 extends close to the inlet passage of reaction gas and up to the vicinity of the substrate, whereby the inside of the passage is maintained at a very good plasma state, so that the evaporated substance dissolved and ionized by the HCD beam goes straight on the substrate 13 and hence

the deposition efficiency is considerably enhanced. Further, 23 is a voltage applied device for reaction gas, which is provided with a cooling tube 24 and an inlet tube 25 made from Ta. The ionization of the reaction gas can be promoted by applying a voltage to the inlet tube 25.

Moreover, the ion plating conditions through ECD method using the apparatus of the drawing were acceleration voltage of 75 V, current of 1000 A and vacuum degree of 7.5×10^{-4} Torr. In addition, the preliminary heating temperature was 400°C and the applied voltage was 60 V.

④ After Ti coating of $0.5 \mu\text{m}$ in thickness was deposited onto the steel sheet surface with the ion plating apparatus shown in Fig. 1, TiN ceramic coating ($0.5 \mu\text{m}$ thickness) was further formed thereon. Moreover, the coating formation conditions were the same as in the above item ③.

⑤ TiN coating of $1 \mu\text{m}$ was formed by ion plating treatment through the conventional ECD method using an ion plating apparatus shown in Fig. 2. In this case, the treating conditions were acceleration voltage of 70 V, current of 1000 A and vacuum degree of 7×10^{-4} Torr. The preliminary heating temperature was 400°C and the applied voltage was 60 V.

In this drawing, 26 is a substrate, 27 a tube

for reaction gas, 28 a crucible, 29 an evaporation source (Ti), 30 a usual L-shaped HCD gun, and 31 a focusing coil.

⑥ After Ti coating of 0.5 μm in thickness was formed by using the ion plating apparatus shown in Fig. 2, TiN coating of 0.5 μm in thickness was further formed thereon. Moreover, the treating conditions were the same as in the item ⑤.

The uniformity, corrosion resistance, adhesion property, smoothness and densifying degree (porosity) of the coatings obtained by the above treatments were measured to obtain results as shown in Table 1.

Table 1

Condition	Ion plating method	Evaporation rate ($\mu\text{m}/\text{min}$)	*1: Uniformity	*2: Corrosion resistance	*3: Adhesion property	*4: Smoothness	*5: Porosity
①	Formation of TiN (1 μm thickness) by EB+RF	0.6	± 35	x	x	x	x
②	Formation of TiN (0.5 μm thickness) by EB+RF after the formation of Ti (0.5 μm thickness) by EB	0.6~0.7	± 35	Δ	x	x	x
③	Formation of TiN (1 μm thickness) by a method of Fig. 1	2.5	± 20	Δ	Δ	O	O
④	Formation of TiN (0.5 μm thickness) after the formation of Ti (0.5 μm thickness) by a method of Fig. 1	2.5~2.7	± 20	O	O	O	O
⑤	Formation of TiN (1 μm thickness) by a method of Fig. 2	1.0	± 30	Δ	Δ	x	Δ
⑥	Formation of TiN (0.5 μm thickness) after the formation of Ti (0.5 μm thickness) by a method of Fig. 2	1.0~1.2	± 30	Δ	Δ	Δ	Δ

*1: The difference in thickness between central portion and end portion is represented by %.

*2: spraying test with saline solution: 3.5% saline solution, 35°C, spraying for

4 hours-drying for 1 hour x 3 cycles

x: corrosion Δ : somewhat corrosion O: no corrosion

*3: 360° bending after high temperature annealing

x: full peeling, Δ : somewhat peeling, O: no peeling

*4: observation with scanning microscope

x: $R_a > 0.4 \mu\text{m}$, O: $R_a \leq 0.4 \mu\text{m}$

*5: Ferroxy test (number of pores per 1 cm^2)

x: many (10 or more) Δ : small (9-2) O: very few (1 or less)

As seen from the above table, when the Ti coating is formed according to the method of the invention in ④ and further the TiN coating is formed thereon, all of the evaporation rate, uniformity of coating, corrosion resistance, adhesion property, smoothness and densifying degree are excellent as compared with the others ①, ②, ③, ⑤ and ⑥. Particularly, it is noticed that the corrosion resistance and adhesion property are excellent in the case of forming the TiN coating on the Ti coating layer as compared with the case ③ of directly forming TiN on the steel sheet surface.

As to the invention method ④, the formation state of the ceramic coating was further minutely investigated by using an electron microscope, and as a result it has been found that the formation state of the coating largely changes in accordance with the conditions of forming the high plasma atmosphere or the difference of making power for the focusing coil located on the passage of moving evaporated substance.

In Fig. 3 are shown results measured on a relationship between making power for focusing coil and making power for HCD beam in order to obtain a smooth ceramic coating.

As seen from this drawing, in order to obtain the smooth ceramic coating, the making powers for

focusing coil and HCD beam are existent within proper ranges, respectively, and it is necessary to adjust the making power for focusing coil in accordance with the making power for HCD beam. That is, it has been found that the following conditions should be satisfied:

$$30 \leq H \leq 160$$

$$0.2+0.03H \leq F \leq 5.5+0.075H$$

, where H: making power for HCD beam (kW)

F: making power for focusing coil (kW).

This is considered as follows:

That is, the good ceramic coating is obtained only by making an optimum plasma atmosphere. If the making power for focusing coil is too small, the high plasma atmosphere can not be generated, so that the coating becomes uneven and rough, while if the making power for focusing coil is too large, the magnetic field becomes extremely strong only at the central portion so as not to generate a favorable plasma atmosphere.

In any case, the smooth ceramic coating can not be obtained. Therefore, in order to obtain the smooth ceramic coating, it is important to satisfy the above ranges. Moreover, the reason why the making power H for HCD beam in the above equation is limited to the above range is as follows. That is, when the making power for HCD beam is less than 30 kW, the ionization energy to the evaporated amount becomes lacking and the good

plasma atmosphere can not be formed, while when it exceeds 160 kW, the beam is scattered by the evaporated substance and the evaporation energy is degraded.

As to such an improvement of the adhesion property, corrosion resistance and further smoothness, it has been found that the corrosion resistance, adhesion property and further smoothness can largely be improved by forming onto the steel sheet surface a metal or semimetal coating as a first layer and a ceramic coating as a second layer under particular treating conditions likewise a case that when different metals are dry plated to form two-layer coatings under a super vacuum of not more than 1×10^{-5} Torr, which is really impossible in industrial scale on the surface-treated steel sheet, the considerable improvement of corrosion resistance is recognized as compared with that of the single layer coating as mentioned above. Therefore, the invention is very useful in the production of practically used ceramic coated steel sheets.

In this connection, it has hitherto been known to form ceramic coating of TiN, CrN or the like as 1-2 layer by using the spraying method. However, the number of pores is large in the ceramic coating through the spraying method as compared with the coating formed under vacuum, and also the smoothness is very poor, so that the coating having a rich smoothness of not more

than 0.4 μm as a center-line average roughness can not be obtained at all.

According to the invention, in order to improve the adhesion property between steel sheet and ceramic coating in addition to the improvement of corrosion resistance through the formation of metal-ceramic coating, it is desirable that the preliminary heating temperature is raised to 100-600°C and the applied voltage is used within a range of 10-200 V.

Then, a hot rolled sheet of stainless steel containing C: 0.015%, Mn: 0.35%, Cr: 18.8% and Si: 0.13% (2.3 mm thickness) was subjected to cold rolling - heat treatment to a thickness of 0.25 mm, and (A) Cr of 2.0 μm in thickness or (B) Cr of 1.0 μm in thickness was formed onto the steel sheet surface by wet plating. As to (B), the Cr coating was further subjected to a dry plating shown by (a) - (d).

(a) TiN was formed at a thickness of 1.0 μm by EB+RF;

(b) TiN was formed at a thickness of 1.0 μm by the method of Fig. 1;

(c) Ti (0.5 μm thickness) was formed by the method of Fig. 1 and TiN (0.5 μm thickness) was further formed thereon;

(d) Ti (0.5 μm thickness) was formed by the method of Fig. 2 and TiN (0.5 μm thickness) was further formed

thereon.

The evaporation rate, uniformity, corrosion resistance, adhesion property, smoothness and densifying degree of the thus obtained ceramic coatings were measured to obtain results as shown in Table 2.

Table 2

	Wet plating	Ion plating treatment	Evaporation rate (µm/min)	*1 Uni-Formity	*2 Corrosion resistance	*3 Adhesion property	*4 Smoothness	*5 Porosity
(A)	Cr plating at a thickness of 2.0 µm	none	-	-	x	x	x	x
(B)	Cr plating at a thickness of 1.0 µm	(a)	0.6	±35	x	x	x	x
		(b)	2.6	±20	Δ	○	○	○
		(c)	2.8	±20	○	○	○	○
		(d)	1.0	±30	Δ	○	Δ	Δ

*1: The difference in thickness between central portion and end portion is represented by %.

*2: spraying test with saline solution: 3.5% saline solution, 35°C, spraying for

4 hours-drying for 1 hour x 6 cycles

x: fairly corrosion, Δ: somewhat corrosion, ○: no corrosion

*3: 360° bending after high temperature annealing

x: full peeling, Δ: somewhat peeling, ○: no peeling

*4: observation with scanning microscope

x: Ra>0.4 µm, ○: Ra≤0.4 µm

*5: Ferroxy test (number of pores per 1 cm²)

x: many (10 or more) Δ: small (9-2) ○: very few (1 or less)

As seen from Table 2, when the Cr coating is formed by the wet plating and the TiN coating is further formed thereon according to the method (c) of the invention, all of the evaporation rate, coating uniformity, corrosion resistance, adhesion property, smoothness and densifying degree are excellent as compared with those of the other (a), (b) and (d) as well as the case of no ion plating.

Next, a hot rolled sheet of stainless steel containing C: 0.015%, Mn: 0.15%, Cr: 18.5% and Ni: 8.6% (2.3 mm thickness) was subjected to cold rolling - recrystallization annealing to form a sheet of 0.25 mm in thickness, and thereafter the surface was degreased. Then, the steel sheet surface was subjected to the following coating treatments (a) - (c) through ① ECD method, ② (EB+RF) method and ③ spraying method, whereby TiC or TiO₂ coating was formed as an outermost layer.

(a) Cr of 0.5 μm was formed and TiC of 1.5 μm was formed thereon;

(b) Cr of 0.5 μm was formed, and TiC of 0.5 μm was formed, and further TiO₂ of 1.0 μm was formed;

(c) Cr of 0.5 μm was formed, and TiC of 1.5 μm was formed, and the annealing was further carried out at 800°C in an oxidizing atmosphere.

The wavelength dependency of radioactivity at

600°C (surface temperature of sample) was measured to obtain results as shown in Fig. 4, while the adhesion property, peeling properties at rapid heating and rapid cooling and radioactivity at a wavelength of 7 μm every the above condition were measured to obtain results as shown in Table 3.

Table 3

	Method	Coating method	*1 Adhesion property	*2 Peeling property	*3 Radiation property
①	HCD method (Invention)	(a) Cr of 0.5 μm was formed and TiC of 1.5 μm was formed thereon	O	O	0.7
		(b) Cr of 0.5 μm was formed, and TiC of 0.5 μm was formed, and further TiO ₂ of 1.0 μm was formed	O	O	0.8
		(c) Cr of 0.5 μm was formed, and TiC of 1.5 μm was formed, and the annealing was further carried out at 800°C in an oxidizing atmosphere	O	O	0.8
②	(EB+RF) method	(a) Cr of 0.5 μm was formed and TiC of 1.5 μm was formed thereon	Δ	Δ	0.6
		(b) Cr of 0.5 μm was formed, and TiC of 0.5 μm was formed, and further TiO ₂ of 1.0 μm was formed	Δ	x	0.6
		(c) Cr of 0.5 μm was formed, and TiC of 1.5 μm was formed, and the annealing was further carried out at 800°C in an oxidizing atmosphere	Δ	Δ	0.6
③	Spraying method	(a) Cr of 0.5 μm was formed and TiC of 1.5 μm was formed thereon	x	x	0.6
		(b) Cr of 0.5 μm was formed, and TiC of 0.5 μm was formed, and further TiO ₂ of 1.0 μm was formed	x	Δ	0.6
		(c) Cr of 0.5 μm was formed, and TiC of 1.5 μm was formed, and the annealing was further carried out at 800°C in an oxidizing atmosphere	x	Δ	0.7

*1: 90° bending properties (repeat 4 times)

O: no peeling Δ : somewhat peeling x: peeling

*2: Peeling properties through rapid heating and rapid cooling treatments

O: no peeling Δ : somewhat peeling x: peeling

*3: radioactivity at sample temperature (600°C) and wavelength of 7 μm

As seen from Table 3 and Fig. 4, in the case ① formed through the HCD method, the adhesion property, peeling properties and radiation property are good in the all conditions (a) - (c) as compared with the cases formed by the other methods ② and ③.

Moreover, in the case ①, the radiation property is excellent in the conditions (b) and (c) than the condition (a).

As mentioned above, when the coating is formed by using the HCD method, the ionization ratio is as high as 40-60% as compared with the other (EB+RF) method or the spraying method, so that the quality of the coating can be densified, from which it is considered to obtain materials having improved uniformity, adhesion property, smoothness and radiation property.

As a starting material used in far-infrared radiating material according to the invention, it is favorable to use low carbon steel sheets and stainless steel sheets, particularly relatively thin steel sheets (0.1-1.5 mm thickness) capable of performing mass production and rendering into a shape suitable for use purpose and being inexpensive in the cost and having an electric conductivity.

These steel sheets are usually produced through hot rolling, cold rolling and annealing treatment steps and then greased or further rendered into a mirror state

of $Ra \leq 0.4 \mu\text{m}$ by a polishing treatment. Thereafter, the surface of each of these steel sheets is subjected to a coating through the HCD method. In this case, according to the invention, it is required to coat at least one of metals and semimetals such as Ti, Cr, Al, Ni, Si, B and the like at a thickness of about $0.1\text{-}5 \mu\text{m}$ in order to provide a good adhesion property to the steel sheet. Next, a ceramic coating of about $0.1\text{-}3 \mu\text{m}$ in thickness is formed on the metal-semimetal coating through the HCD method.

In this case, it is more advantageous to preliminarily heat the steel sheet at $100\text{-}600^\circ\text{C}$ prior to the formation of the above first layer of metal-semimetal coating in view of the improvement of the properties.

In order to obtain good far-infrared radiating properties, it is preferable that at least one oxide of Ti, Cr, Al, Ni, Si and B is further formed at a thickness of about $0.1\text{-}5 \mu\text{m}$ as an outermost layer through the HCD method or the steel sheet is annealed in an oxidizing atmosphere at $500\text{-}1200^\circ\text{C}$ to form an oxide coating.

The coating treatment through the HCD method may be carried out by the usual batch type apparatus. Apart from this, there may be utilized a method of successively coating metal-semimetal onto the steel

sheet surface, and further forming nitride, carbide and oxide layer thereon by the continuous coating equipment (Air-to-Air apparatus).

Particularly, when the steel sheet is used as a far-infrared radiation heating element, it is favorable to use a high melting substance such as Cr, Ni or the like as a metal-semimetal coating formed by wet plating method.

In the invention, it is important that the metal or semimetal coating is formed as an underground layer prior to the formation of ceramic coating onto the steel sheet surface, whereby the considerable improvement of corrosion resistance and adhesion property is achieved.

According to the invention, the moving passage of the evaporated substance is surrounded by the focusing coil, whereby the inside of the moving passage of the evaporated substance becomes at a good plasma state and stray vapor becomes less, and consequently the deposition onto the substrate can effectively be conducted. Furthermore, since plasma is locked inside the moving passage of the evaporated substance surrounded by the focusing coil, there is caused no wasteful discharge in the ion plating apparatus and the bias voltage can stably be applied to the substrate, so that the adhesion property of the ceramic coating is improved and also the coating becomes dense to improve

the corrosion resistance and smoothness.

From the results of the above experiments, it is clear that the metal-semimetal coating is formed as a first layer onto the steel sheet surface by the HCD method according to the invention, and then the ceramic coating is formed thereon, whereby the coatings entirely different from the coating through other ion plating methods and having good adhesion property, smoothness and corrosion resistance are obtained.

Moreover, the above effects are made equal or more by previously subjecting the steel sheet surface to a wet plating and further a subsequent oxidation treatment.

In the adaptation of the HCD method according to the invention, HCD guns are arranged side by side over a widthwise direction of the steel sheet to ensure the evaporation amount and uniformity, which can be applied to coils having a width of not less than 500 mm. Particularly, in the invention, it is important to effectively adhere the evaporated atom to the substrate when the evaporated substance is ionized by means of the HCD gun, and therefore, it is essential that the focusing coil is extended from the crucible to the vicinity of the substrate to form a good plasma state inside the focusing coil. Moreover, a distance from the upper end of the focusing coil to the substrate is

preferable to be about 50-150 mm. In this case, it is important to conduct the supply of power into the focusing coil within the range shown in Fig. 3.

In case of ensuring the adhesion property, corrosion resistance of coating and uniformity of the metal-semimetal coating and further the ceramic coating formed on the substrate or the wet plated substrate, the steel sheet is subjected to a preliminary heating at a temperature of 100-600°C prior to the formation of the coating, or a voltage of 10-200 V is applied to the steel sheet during the coating, or both the treatments are conducted.

Moreover, the preliminary heating before the coating is usually carried out by using electron beam, or may be conducted by using an infrared ray or usual resistance heating.

Further, when the voltage of 10-200 V is applied to the steel sheet, it is more advantageous that a high voltage of 50-200 V is used at a first half stage of the coating and a low voltage of 10-50 V is used at a last half stage of the coating from a viewpoint of the improvement of the coating adhesion property.

It is favorable that the steel sheet surface is completely degreased or, if necessary, the steel sheet surface is rendered into a mirror state by mechanical polishing or chemical-electrolytic polishing prior to

the ion plating treatment. The metal and/or semimetal coating is formed on such a mirror finished surface.

According to the invention, it is possible to form a coating having an excellent adhesion property without conducting a usual bombardment treatment. In this case, after a passivate coating is formed by the aforementioned electrolytic treatment with nitric acid, the metal and/or semimetal coating may be formed.

As the metal and semimetal, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Co, Cu, Zn, Al, B and Si are effectively adaptable.

In this case, the coating thickness is favorable to be about 0.1-5 μm .

Then, the ceramic coating is further formed on the metal-semimetal coating.

As the ceramic coating, at least one selected from nitrides, carbides and carbonitrides of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Co, Ni, Al, B and Si and oxides of Al, Zn, Mn, Mg, Ti, Cr, B, Ni and Si is preferable. In this case, the coating thickness is desirable to be about 0.1-5 μm .

Although there is mainly described with respect to the case of forming two layer coatings consisting of metal-semimetal coating as a first layer and ceramic coating as a second layer, the invention is not intended as limitation thereof, and a further ceramic coating may

be formed on the above two layers through the presence or absence of a metal-semimetal coating. That is, a ceramic coating may be formed as a third layer, or a metal-semimetal coating may be formed as a third layer and a ceramic coating may be formed as a fourth layer, or further the formation of such coating may be repeated. In brief, in the invention, the metal-semimetal coating is formed as an innermost layer and the ceramic coating is formed as an outermost layer.

Moreover, the coated steel sheets obtained according to the invention can be used as a far-infrared radiation heating element. In this case, it is preferable that the ceramic coating of oxide is formed as an outermost layer or the annealing is carried out in an oxidizing atmosphere of 500-1200°C after the formation of the ceramic coating.

In the deposition of metal-semimetal and ceramic through the ECD method, an apparatus of continuous vacuum line is usually used, but a batch type evaporation apparatus of a large capacity may be used.

In the invention, low carbon cold rolled steel sheets or stainless steel sheets capable of providing a wide area and being relatively cheap are advantageously adapted as the substrate.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic view of a batch type ion plating apparatus applied to the invention;

Fig. 2 is a schematic view of the conventional ion plating apparatus;

Fig. 3 is a graph showing a relationship between making power for HCD beam and making power for focusing coil upon the quality of the ceramic coating; and

Fig. 4 is a graph showing a wavelength dependency of radioactivity at a surface temperature of 600°C.

BEST MODE OF CARRYING OUT THE INVENTION

Example 1

A hot rolled sheet of stainless steel containing C: 0.038%, Si: 0.12%, Mn: 1.0%, Cr: 17.5% and Mo: 1.4% (2.2 mm thickness) was cold rolled to a thickness of 0.3 mm and subjected to an annealing treatment, from which a specimen of 500 mm × 500 mm was cut out as a substrate. After the surface of the substrate was degreased, a coating selected from various metals and semimetals was formed on the surface at a thickness of 0.5 μm by an ion plating treatment using an apparatus shown in Fig. 1 and then various ceramic coatings were formed thereon at a total thickness of 1.0 μm, and further third and fourth layers were formed on a part of the product. The adhesion property, smoothness,

corrosion resistance and densifying degree of the thus obtained products were measured. The results are shown in Table 4.

Moreover, the conditions of the ion plating treatment were acceleration current: 1000 A, acceleration voltage: 70 V, vacuum degree: 7×10^{-4} Torr, voltage and current of focusing coil: 10 V, 800 A, bias voltage: 80 V and preliminarily heating temperature: 500°C.

Table 4(a)

No.	Remarks	Kind of coatings				Adhesion property 360° bending property *1	Smoothness surface property *2	Corrosion resistance spraying test with saline solution *3	Porosity ferroxyl test *4
		first layer	second layer	third layer	fourth layer				
(1)		Ti	ZrN			○	○	○	
(2)		Ti	HfN			○	○	○	
(3)		Ti	VN			○	○	○	
(4)		Ti	NbN			○	○	○	
(5)		Cr	TaN			○	○	○	
(6)	nitrides	Cr	CrN			○	○	○	
(7)		Cr	MoN	CrN		○	○	○	
(8)		Ni	NiN	TiN		○	○	○	
(9)		Ni	AlN	Ni	AlN	○	○	○	
(10)		(Ti+Al)	Si ₃ N ₄			○	○	○	
(11)		(Ti+Al)	BN			○	○	○	
(12)			Ti	TiC			○	○	
(13)			Ti	HfC			○	○	
(14)			Ti	VC			○	○	
(15)	carbides	Cr	NbC			○	○	○	
(16)		Cr	MoC			○	○	○	
(17)		V	SiC	TiC		○	○	○	
(18)		Zr	BC	Ti	TiC	○	○	○	

Table 4(b).

No.	Remarks	Kind of coatings				Adhesion property 360° bending property *1	Smoothness surface property *2	Corrosion resistance spraying test with saline solution *3	Porosity ferroxyl test *4
		first layer	second layer	third layer	fourth layer				
(19)	carbonitrides	Ti	Ti (CN)			○	○	○	
(20)		Cr	Cr (CN)			○	○	○	
(21)	oxides	V	TiO ₂			○	○	○	
(22)		Mn	Al ₂ O ₃			○	○	○	
(23)		Cu	SiO ₂			○	○	○	
(24)		Ni	ZnO			○	○	○	
(25)		Co	MgO	Al ₂ O ₃		○	○	○	
(26)		B	MnO	Ni	TiO ₂	○	○	○	

*1 ... x: full peeling, Δ: somewhat peeling, ○: no peeling

*2 ... x: Ra > 0.4 μm, ○: Ra ≤ 0.4 μm

*3 ... Δ: somewhat corrosion, ○: no corrosion
(35% saline solution, 35°C, spraying for 4 hours - drying for 1 hour x 6 cycles)

*4 ... ferroxyl test (pore number per 1 cm²)
x: many (more than 10), Δ: small (9-2), ○: very few (1 or less)

Example 2

A cold rolled sheet of a low carbon steel containing C: 0.044%, Si: 0.01%, Mn: 0.33%, P: 0.009% and S: 0.011% (a hot rolled sheet of 2.2 mm in thickness was cold rolled to a thickness of 0.7 mm) was subjected to a recrystallization annealing at 680°C for 10 hours. Thereafter, the surface of the steel sheet was polished to a center-line average roughness Ra of 0.2 μm by electrolytic polishing, onto which were formed a metal-semimetal coating (0.7 μm thickness) and a ceramic coating (0.7-0.8 μm thickness), each being made from a substance shown in Table 5, by using the apparatus shown in Fig. 1 under conditions of HCD acceleration voltage: 80 V, acceleration current: 1000 A, vacuum degree: 8×10^{-4} Torr, focusing coil: 7 V, 600 A, bias voltage: 70 V and preliminarily heating temperature: 450°C.

Moreover, as to numerals (1), (5), (9), (13), (16) and (20) in Table 5, a Ni thin coating of 0.5 μm in thickness was formed on the steel sheet surface by wet plating prior to the dry plating.

The adhesion property, smoothness, corrosion resistance and densifying degree of the obtained products were measured to obtain results as shown in Table 5.

Table 5(a)

No.	Kind of ceramic compound	Presence or absence of wet plating	Coatings		Adhesion property 180° bending at 20 mm (room temperature) △ somewhat peeling ○ no peeling	Smoothness observation by scanning electron microscope (room temperature) △ somewhat unevenness ○ no unevenness	Corrosion resistance spraying test with saline solution (*) △ somewhat corrosion ○ no corrosion	Porosity ferroxyl test (**)
			first layer	second layer				
(1)		presence	Al+Cr+Ti	TiN-MnN	○	○	○	○
(2)	nitrides	absence	Cr	TiN-CrN-NiN	○	○	△	○
(3)		absence	Ti+Al	Ti(CN)-AlN-Si ₃ N ₄	○	△	○	○
(4)		absence	Cr+Al	HfN-NiN-BN-Si ₃ N ₄	△	○	△	○
(5)		presence	Ti	CrC-VC	○	○	○	○
(6)	carbides	absence	Cr	TiC-VC	○	○	○	○
(7)		absence	Ti	SiC-TiC-MnC	△	○	△	○
(8)		absence	Cr	VC-CoC-NiC-AlC	△	○	△	○
(9)		presence	Ti	Al ₂ O ₃ -SiO ₂	△	○	○	○
(10)		absence	Cr	MgO-Al ₂ O ₃	○	○	○	○
(11)	oxides	absence	Ti+Si	SiO ₂ -Al ₂ O ₃ -ZnO	△	△	△	○
(12)		absence	Cr+B	ZnO-Al ₂ O ₃ -MnO-TiO ₂	△	△	△	○

Table 5(b)

No.	Kind of ceramic compound	presence or absence of wet plating	Coatings		Adhesion property 180° bending at 20 mm (room temperature) Δ somewhat peeling ○ no peeling	Smoothness observation by scanning electron microscope (room temperature) Δ somewhat unevenness ○ no unevenness	Corrosion resistance spraying test with saline solution (*) Δ somewhat corrosion ○ no corrosion	Porosity ferroxyl test (**)
			first layer	second layer				
(13)	nitrides and carbides	presence	Zr	Ti(CN)-VC	○	○	○	○
(14)		absence	V	TiC-ZN-WN	Δ	○	Δ	○
(15)		absence	Mn+Cr	TiN-VC-CrN-CrC	○	○	○	○
(16)	nitrides and oxides or carbides and oxides	presence	Ti	TiN-Al ₂ O ₃	○	○	○	○
(17)		absence	Ti	TiN-Al ₂ O ₃ -VN	Δ	Δ	Δ	○
(18)		absence	Cr	TiC-SiO ₂	○	Δ	Δ	○
(19)		absence	Cr	VC-SiO ₂ -ZrC	Δ	○	○	○
(20)	nitrides, carbides and oxides	presence	Ti+Cr	TiN-Al ₂ O ₃ -VC	Δ	○	○	○
(21)		absence	Al+Cr	VN-SiO ₂ -VC-MgO	Δ	Δ	Δ	○
(22)		absence	Al+Cr+Ti	VC-SiO ₂ -Al ₂ O ₃ -TiN	○	Δ	Δ	○

(*) spraying test with saline solution: 3.5% saline solution, spraying for 4 hours, drying for 1 hour X 3 cycles
 (**) ferroxyl test (pore number per 1 cm²) X many (10 or more) Δ small (9-2) ○ very few (1 or less)

Example 3

A hot rolled sheet (2.3 mm thickness) of stainless steel containing C: 0.04%, Mn: 1.2%, Si: 0.08%, Cr: 17.2% and Ni: 8.9% was finished to a thickness of 0.25 mm through cold rolling and heat treatment. Thereafter, the steel sheet surface was degreased and Cr, Ni and Ti were coated onto the steel sheet surface at respective thickness of 0.5 μm by HCD method.

Then, coatings of various nitride-carbide were formed at a thickness of 1.5-3.0 μm . Thereafter, a part of the samples was subjected to a coating treatment of various oxides (1.5 μm thickness) or to an annealing treatment in an oxidizing atmosphere of 800°C.

The adhesion property, peeling properties at rapid heating-rapid cooling and radiation properties (radioactivity at surface temperature of 650°C and wavelength of 7 μm) of the thus obtained products were measured to obtain results as shown in Table 6.

Table 6

No.	First layer	Second layer (thickness)	Third layer (thickness)	Oxidation treatment	*1 Adhesion property	*2 Peeling property	*3 Radiation property
1	Cr	TiN (1.5 μm)	SiO ₂ (1.5 μm)	—	○	○	0.8
2	Cr	AlN (")	TiO ₂ (")	—	○	○	0.8
3	Cr	Si ₃ N ₄ (")	CrO ₂ (")	—	○	△	0.7
4	Cr	TiC+BN (")	TiO ₂ +SiO ₂ (")	—	○	○	0.8
5	Ni	CrC+Si ₃ N ₄ (")	SiO ₂ +NiO (")	—	△	○	0.9
6	Ni	TiC (")	Al ₂ O ₃ (")	—	○	△	0.8
7	Ni	Si ₃ N ₄ +TiC (")	CrO ₃ (")	—	○	○	0.8
8	Ni	NiC+TiC (")	NiO+Al ₂ O ₃ (")	—	○	○	0.8
9	Ti	CrC+AlN (")	Al ₂ O ₃ (")	—	○	○	0.9
10	Ti	Si ₃ N ₄ +BN+AlN (")	NiO+Al ₂ O ₃ +NiO (")	—	○	○	0.7
11	Ti	NiC+SiC+AlN (")	SiO ₂ +Al ₂ O ₃ +TiO ₂ (")	—	○	△	0.9
12	Ti	TiN+Ti(C,N)+BN+AlN (")	TiO ₂ +CrO ₂ (")	—	△	○	0.9
13	Cr	TiN (3.0 μm)	—	oxidizing atmosphere of 800°C	○	○	0.8
14	Cr	Ti(C,N) (")	—	"	○	△	0.8
15	Cr	TiN+CrN (")	—	"	○	○	0.8
16	Ni	AlN+TiC (")	—	"	○	○	0.8
17	Ni	CrC (")	—	"	○	○	0.7
18	Ni	BN+AlN+TiC (")	—	oxidizing atmosphere of 1000°C	△	○	0.7
19	Ti	AlN+CrN+TiN (")	—	"	○	○	0.8
20	Ti	NiC+AlN+SiC (")	—	"	△	○	0.9
21	Ti	BN+AlN+TiC+CrC (")	—	"	○	○	0.8

*1 90° bending property (repeat 4 times) ○: no peeling △: somewhat peeling x: peeling

*2 Peeling properties at rapid heating-rapid cooling

○: no peeling △: somewhat peeling x: peeling

*3 radioactivity at sample temperature (600°C) and wavelength of 7 μm

INDUSTRIAL APPLICABILITY

According to the invention, there can be obtained steel sheets being dense in the surface and hence excellent in all of adhesion property, smoothness, uniformity and corrosion resistance, and consequently these steel sheets can be applied to use applications requiring various surface properties inclusive of wear resistance and corrosion resistance.

CLAIMS

1. A steel sheet provided with a dense ceramic coating having improved adhesion property, smoothness and corrosion resistance, comprising an underground coating formed on a surface of a low carbon steel sheet or a stainless steel sheet and made from at least one of metals and semimetals, and a ceramic coating of at least one layer formed on said underground coating; said ceramic coating having a surface roughness R_a of not more than $0.4 \mu\text{m}$ and a pore number per 1 cm^2 of not more than 1.
2. The steel sheet according to claim 1, wherein said metal-semimetal coating is existent between said ceramic coatings.
3. The steel sheet according to claim 1 or 2, wherein said ceramic coating is made from at least one selected from nitrides, carbides or carbonitrides of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Co, Ni, Al, B and Si and oxides of Al, Zn, Mn, Mg, Ti, Cr, B, Ni and Si.
4. A method of producing steel sheets provided with a dense ceramic coating having improved adhesion property, smoothness and corrosion resistance by forming a ceramic coating onto a surface of low carbon steel sheet or stainless steel sheet through an ion plating treatment with HCD method, which comprises forming a metal-semimetal coating made from at least one of metals

and semimetals as a first layer onto said surface of said steel sheet and forming a ceramic coating as a second layer on said coating under the following conditions using as a moving passage of an evaporation substance an inside of a focusing coil arranged so as to surround an outer periphery of a crucible and extend near to said surface of said steel sheet.

Account

$$30 \leq H \leq 160$$

$$0.2+0.03H \leq F \leq 5.5+0.075H$$

(wherein H: a making power (kW) of ECD beam

F: a making power (kW) of focusing coil)

5. The method of producing steel sheets according to claim 4, wherein a surface of said steel sheet is subjected to a polishing treatment so as to be $Ra \leq 0.4 \mu\text{m}$ prior to the formation of said metal-semimetal coating as a first layer.

6. The method of producing steel sheets according to claim 4 or 5, wherein said steel sheet is preliminarily heated to 100-600°C prior to the formation of said metal-semimetal coating as a first layer.

7. The method of producing steel sheets according to claim 4, 5 or 6, wherein a surface of said steel sheet is subjected to Cr or Ni plating by wet plating prior to the formation of said metal-semimetal coating as a first layer.

8. The method of producing steel sheets according to claim 4, 5, 6 or 7, wherein the formation of ceramic coating is repeated on said ceramic coating as a second layer through the presence or absence of metal-semimetal coating, if necessary.

9. The method of producing steel sheets according to claim 4, 5, 6, 7 or 8, wherein an annealing treatment is carried out in an oxidizing atmosphere of 500-1200°C after the formation of ceramic coating as a final layer.

10. The method of producing steel sheets according to claim 4, 5, 6, 7, 8 or 9, wherein said ceramic coating is made from at least one selected from nitrides, carbides or carbonitrides of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Co, Ni, Al, B and Si and oxides of Al, Zn, Mn, Mg, Ti, Cr, B, Ni and Si.

FIG. 1

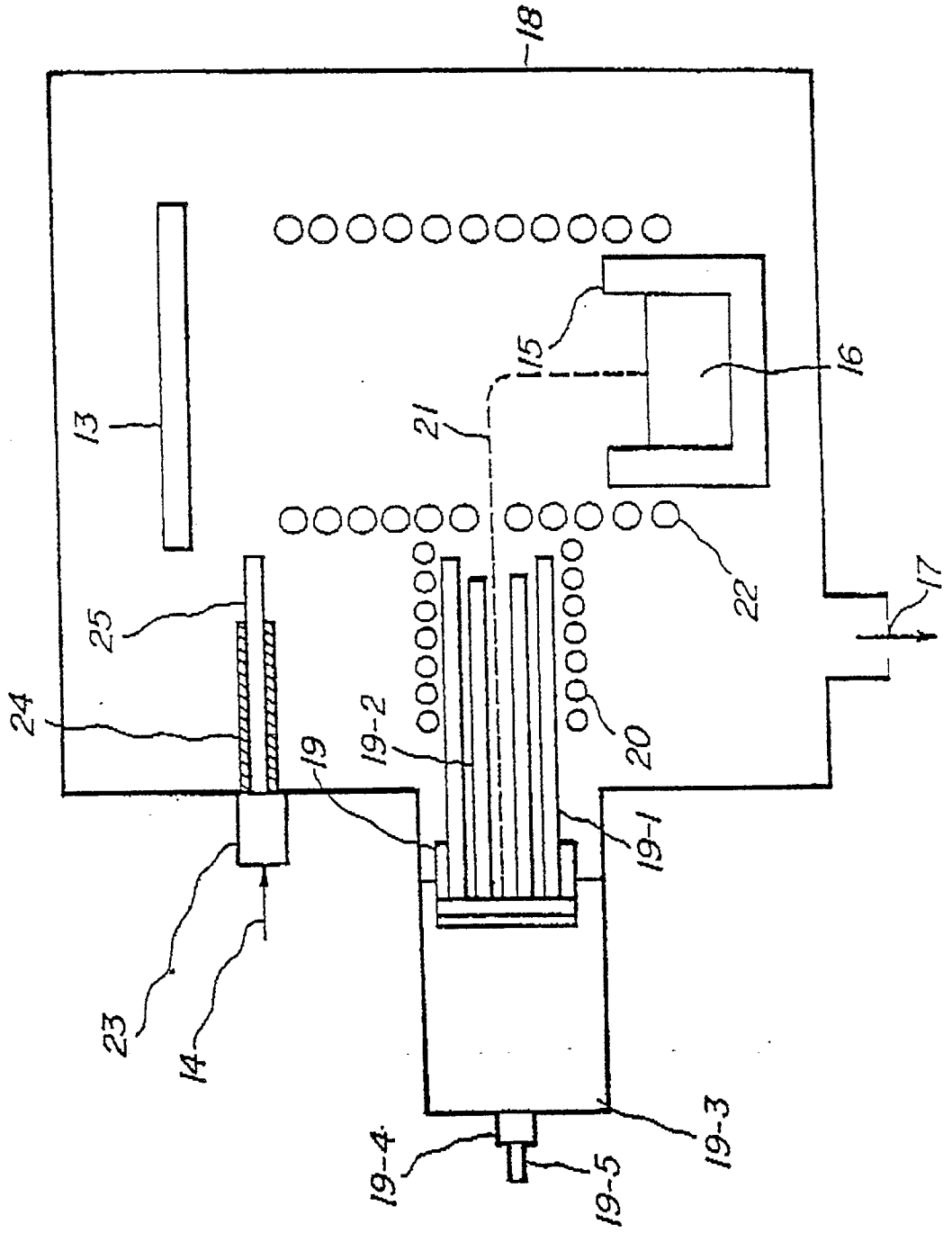


FIG. 2

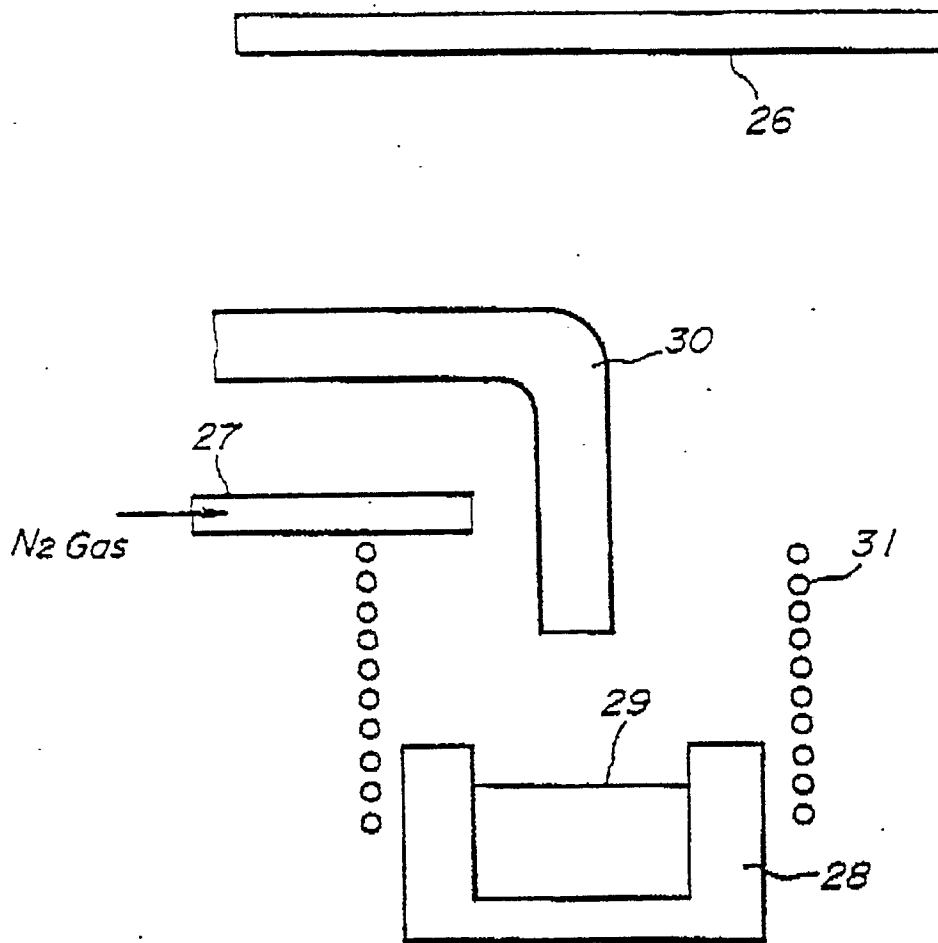


FIG. 3

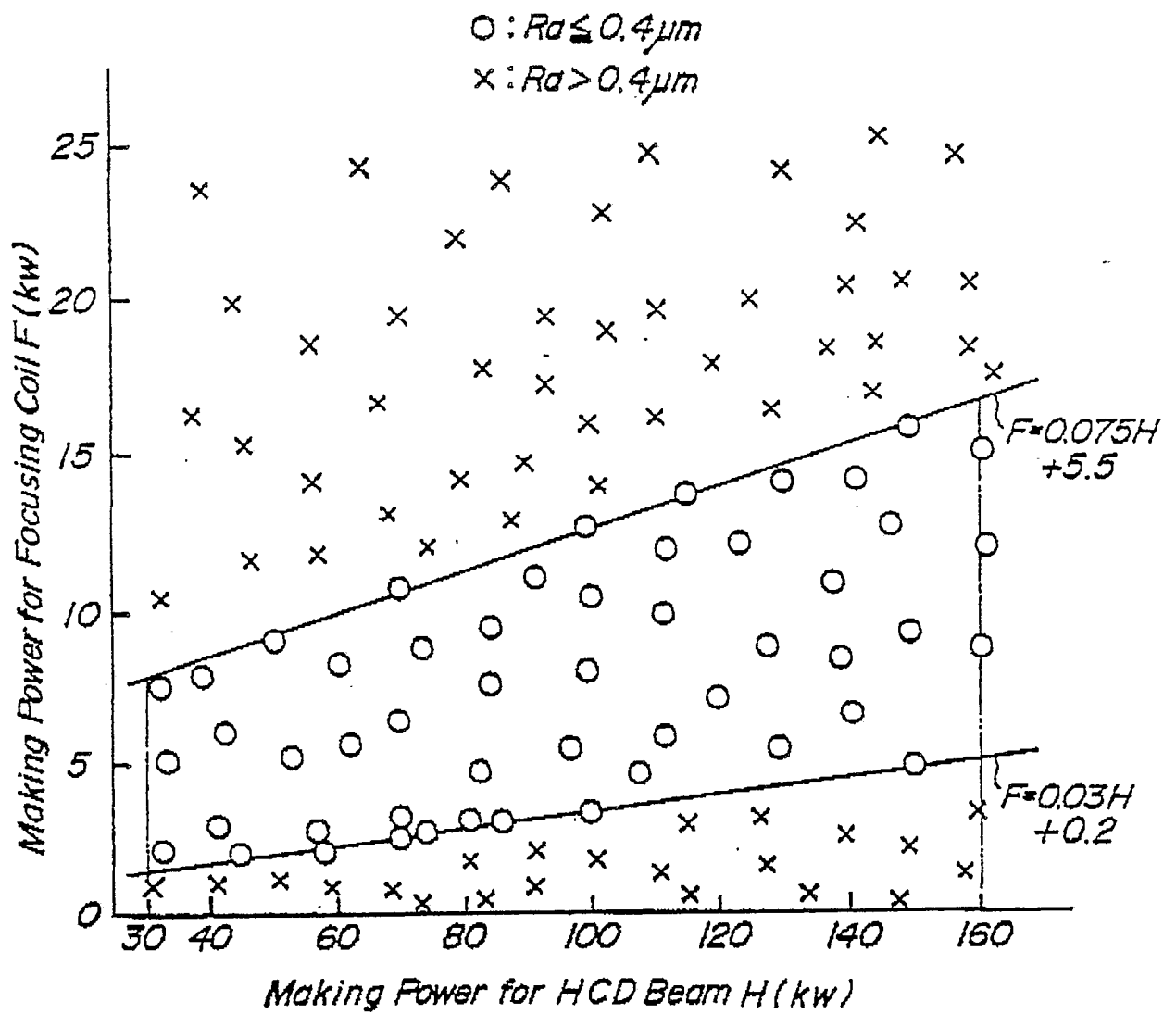
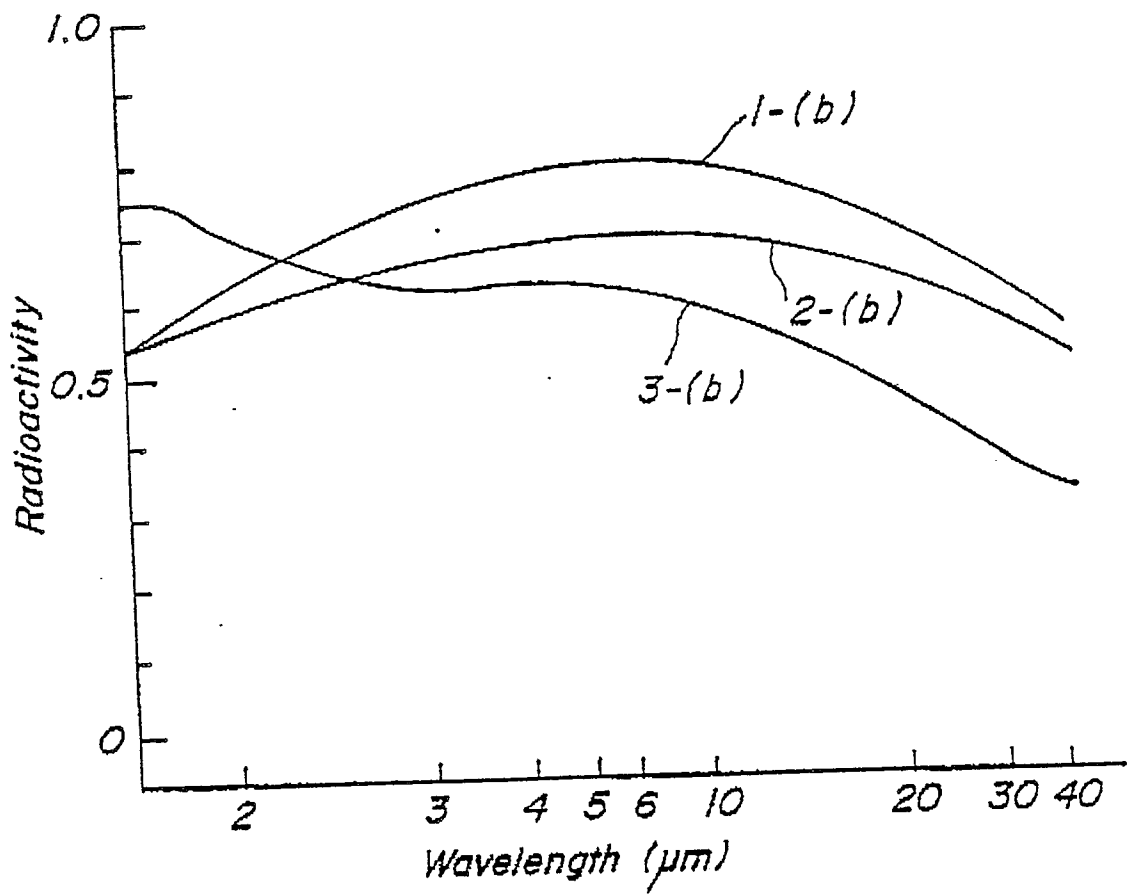


FIG. 4



INTERNATIONAL SEARCH REPORT

International Application No PCT/JP89/00435

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int. Cl ⁴	C23C14/06, 14/32	
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC	C23C14/06, 14/32	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
Jitsuyo Shinan Koho	1926-1989	
Kokai Jitsuyo Shinan Koho	1971-1989	
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category [*]	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	JP, A, 58-96869 (Daini Seikosha Kabushiki Kaisha) 9 June, 1983 (09.06.83) Page 2, upper left column, lines 2 to 5 (Family: none)	1-3
Y	JP, A, 62-151555 (Mitsubishi Heavy Industries, Ltd.) 6 July, 1987 (06.07.87) Page 2, upper right column (Family: none)	1-3
A	JP, A, 52-149275 (Nishida Norio) 12 December, 1977 (12.12.77) Page 2, lower left column (Family: none)	4-10
<p>[*] Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
July 4, 1989 (04.07.89)	July 24, 1989 (24.07.89)	
International Searching Authority	Signature of Authorized Officer	
Japanese Patent Office		